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(71)Applicant : NIPPON OIL CORP

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(54) LUBRICATING OIL COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lubricating oil composition having very excellent maintainability of basic value under NOx atmosphere.

SOLUTION: This lubricating oil composition comprises (A) 0.005-0.5% by mass based on a metal element conversion amount of an alkali metal or an alkaline earth metal salicylate having 2 or less metal ratio, (B) 0.005-0.5% by mass based on the metal element conversion amount of an alkali metal or an alkaline earth metal sulfonate and (C) 0.005-0.5% by mass based on a phosphorus element conversion amount of a phosphorus-containing abrasion-inhibiting agent in a base oil of the lubricating oil, or the components (A) and (B) of the above amount and additionally (D) 0.1% by mass or less based on a sulfur element conversion amount of zinc dithiophosphate in the base oil of the lubricating oil.

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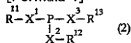
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CLAIMS

[Claim(s)]

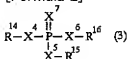
[Claim 1] A metal ratio expressed with the valence x metallic element content (mol) / soap group content of the (A) metallic element (mol) on a constituent whole-quantity standard by lubricant base oil two or less alkaline metal or alkaline-earth-metals salicylate by a metallic element equivalent unit 0.005 - 0.5 mass %, An alkaline metal or alkaline-earth-metals sulfonate by a metallic element equivalent unit (B) 0.005 to 0.5 mass %, And a lubricating oil composition doing 0.005-0.5 mass % content of at least one sort of compounds chosen from a group which consists of phosphorus compounds expressed with the (C) general formula (2), phosphorus compounds expressed with a general formula (3) and those metal salt, or amine salt by a phosphorus element equivalent unit.

[Formula 1]



(In a general formula (2), X^1 , X^2 , and X^3) An oxygen atom or a sulfur atom is shown individually, respectively, and at least one of these is an oxygen atom, and R^{11} , R^{12} , and R^{13} show the hydrocarbon group of a hydrogen atom or the carbon numbers 1-30 individually, respectively.

[Formula 2]

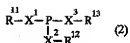


(In a general formula (3), X^4 , X^5 , X^6 , and X^7) An oxygen atom or a sulfur atom is shown individually, respectively, and at least three of these are oxygen atoms, and R^{14} , R^{15} , and R^{16} show the hydrocarbon group of a hydrogen atom or the carbon numbers 1-30 individually, respectively.

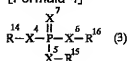
[Claim 2] A metal ratio expressed with the valence x metallic element content (mol) / soap group content of the (A) metallic element (mol) on a constituent whole-quantity standard by lubricant base oil two or less alkaline metal or alkaline-earth-metals salicylate by a metallic element equivalent unit 0.005 - 0.5 mass %, (B) A lubricating oil composition as for which containing an alkaline metal or alkaline-earth-metals sulfonate by a metallic element equivalent unit, and below 0.1 mass % containing 0.005 to 0.5 mass %, and (D) dithiophosphate zinc by a sulfur element equivalent unit.

[Claim 3] Phosphorus compounds expressed with a general formula (2) as a (C) ingredient, phosphorus compounds expressed with a general formula (3), And the lubricating oil composition according to claim 2 doing 0.005-0.5 mass % content of at least one sort of compounds chosen from a group which consists of those metal salt or amine salt by a phosphorus element equivalent unit.

[Formula 3]



(In a general formula (2), X^1 , X^2 , and X^3) An oxygen atom or a sulfur atom is shown individually, respectively, and at least one of these is an oxygen atom, and R^{11} , R^{12} , and R^{13} show the hydrocarbon group of a hydrogen atom or the carbon numbers 1-30 individually, respectively.
[Formula 4]



(In a general formula (3), X^4 , X^5 , X^6 , and X^7) An oxygen atom or a sulfur atom is shown individually, respectively, and at least three of these are oxygen atoms, and R^{14} , R^{15} , and R^{16} show the hydrocarbon group of a hydrogen atom or the carbon numbers 1-30 individually, respectively.

[Claim 4](B) An ingredient is at least a kind of compound chosen from a group which consists of phosphorus compounds expressed with a general formula (3) and its metal salt, or amine salt,

The lubricating oil composition according to claim 1 or 3, wherein all of X^4 [in / in the phosphorus compounds concerned / a general formula (3)], X^5 , X^6 , and X^7 are oxygen atoms and at least one of R^{14} , R^{15} , and R^{16} is a hydrocarbon group of the carbon numbers 1-30.

[Claim 5]A lubricating oil composition given in one paragraph of claims 1 thru/or 4 containing at least one sort chosen from (E) non-ash powder medicine and the (F) antioxidant.

[Claim 6]A lubricating oil composition given in one of paragraphs at claims 1 thru/or 5, wherein sulfur content of lubricant base oil is below 0.005 mass %.

[Claim 7]A lubricating oil composition given in one paragraph of claims 1 thru/or 6, wherein sulfur content of a constituent is below 0.3 mass %.

[Claim 8]A lubricating oil composition given in one paragraph of claims 1 thru/or 7, wherein sulfur content is used for an internal-combustion engine which uses fuel below 50 mass ppm.

[Claim 9]A lubricating oil composition given in one paragraph of claims 1 thru/or 8 using for a gas engine.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the suitable lubricating oil composition for the internal-combustion engines which show the base number maintenance nature excellent also in the bottom of NOx atmosphere in detail about a lubricating oil composition.

[0002]

[Description of the Prior Art] Longed lane-ization of the lubricating oil is further called for from viewpoints of resource effective use in recent years, reduction waste oil's, a lubricating oil user's cost reduction, etc. From the former, in order to improve the longed lane performance of a lubricating oil as base oil of a lubricating oil, Hydrorefining mineral oil refined highly and 1-decene oligomer with little part for aromatic series, or basic nitrogen and sulfur content, In order to raise the oxidation stability [it is especially common to use synthetic oil, such as a polyol ester and aromatic ester, and] under an elevated temperature or NOx atmosphere as an additive agent, Generally it is effective to use it combining oxidation reaction chain terminators, such as peroxide decomposition agents, such as dithiophosphate zinc (ZDTP) and molybdenum dithiocarbamate, a bisphenol system antioxidant, an amine system antioxidant. In the metal system cleaning agent, in order that persalt group nature alkaline-earth-metals salicylate may raise-acid counteraction and oxidation stability; it is used preferably.

[0003] On the other hand as a motor spirit in recent years, from a viewpoint which reduces performance maintenance and particulate matter (PM), such as an exhaust gas cleaning catalyst and DPF (diesel particulate filter). For example, examination to which sulfur content carries out the sulfuric content reduction of gas oil and kerosene which are below 50 mass ppm, or the gasoline further is advanced. Sulfur content is in the tendency which use of the fuel (for example, hydrogen, wood ether and alcohol which do not contain LPG, natural gas, and sulfur content substantially, GTL (Gastouri kid) fuel, etc.) which is below 1 mass ppm also increases. In the internal combustion engine oil which uses such low sulfur fuel, since the mixing amount of the acid for sulfuric acid, such as resulting from sulfur in fuel, etc. decreases, the life of a lubricating oil generally tends to become long.

[0004]

[Problem(s) to be Solved by the Invention] However, the lubricating oil containing comparatively many sulfur content additive agents like ZDTP known as the above-mentioned peroxide decomposition agent, In order that sulfuric acid may generate in a lubricating oil by oxidation or carrying out a pyrolysis in sulfur content additive agent itself, it has turned out that consumption (degradation) of a base number is easy to be accelerated, and the life of a lubricating oil is rash. For this reason, in the lubricating oil containing comparatively many sulfur content additive agents like ZDTP, there is a limit in longed lane-ization of a lubricating oil naturally in optimization of the base oil and the antioxidant which are excellent in oxidation stability, or the place which uses the above-mentioned persalt group nature salicylate further. And the internal-combustion engine which uses especially the above-mentioned low sulfur fuel, especially combustion temperature were high, and it was difficult to advance longed lane-ization of the further lubricating oil in the gas engine exposed to NOx gas. In order to maintain the

performance of the above-mentioned diesel-particulate filter, to be internal combustion engine oil with little sulfur content is also desired.

[0005]Therefore, SUBJECT of this invention achieves optimization of a metal system cleaning agent, an antiwear agent, etc., It is providing the suitable low-sulfur lubricating oil composition for the object for internal-combustion engines using the internal-combustion engine and low sulfur fuel which were extremely excellent in base number maintenance nature, and equipped with the diesel-particulate filter under NOx atmosphere, especially gas engines.

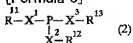
[0006]

[Means for Solving the Problem]In order that this invention persons may solve an aforementioned problem, as a result of repeating examination wholeheartedly, even if it is a low-sulfur lubricating oil composition which does not reduce or contain content of a sulfur content antiwear agent like ZDTP at all, It finds out that a lubricating oil composition in which the base number maintenance characteristic of having excelled extremely under NOx atmosphere by blending combining a specific metal system cleaning agent is shown is obtained, and came to complete this invention.

[0007]As for the first mode of this invention, a metal ratio which is a constituent whole-quantity standard and is expressed with the valence x metallic element content (mol) / soap group content of the (A) metallic element (mol) by lubricant base oil two or less alkaline metal or alkaline-earth-metals salicylate by a metallic element equivalent unit 0.005 - 0.5 mass %, An alkaline metal or alkaline-earth-metals sulfonate by a metallic element equivalent unit (B) 0.005 to 0.5 mass %, And it is in a lubricating oil composition doing 0.005-0.5 mass % content of at least one sort of compounds chosen from a group which consists of phosphorus compounds expressed with the (C) general formula (2), phosphorus compounds expressed with a general formula (3) and those metal salt, or amine salt by phosphorus element conversion.

[0008]

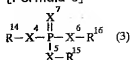
[Formula 5]



[0009](In a general formula (2), X¹, X², and X³) An oxygen atom or a sulfur atom is shown individually, respectively, and at least one of these is an oxygen atom, and R¹¹, R¹², and R¹³ show the hydrocarbon group of a hydrogen atom or the carbon numbers 1-30 individually, respectively.

[0010]

[Formula 6]



[0011](In a general formula (3), X⁴, X⁵, X⁶, and X⁷) An oxygen atom or a sulfur atom is shown individually, respectively, and at least three of these are oxygen atoms, and R¹⁴, R¹⁵, and R¹⁶ show the hydrocarbon group of a hydrogen atom or the carbon numbers 1-30 individually, respectively.

[0012]The 2nd mode of this invention is a constituent whole-quantity standard at lubricant base oil. A metal ratio expressed with the valence x metallic element content (mol) / soap group content of a metallic element (mol) two or less alkaline metal or alkaline-earth-metals salicylate by a metallic element equivalent unit (A) 0.005 to 0.5 mass %, (B) Be in a lubricating oil composition as for which containing an alkaline metal or alkaline-earth-metals sulfonate by a metallic element equivalent unit, and below 0.1 mass % containing 0.005 to 0.5 mass %, and (D) dithiophosphate zinc by sulfur element conversion. Phosphorus compounds further expressed with the 2nd mode by the above-mentioned general formula (2) as a (C) ingredient. It is preferred to do 0.005-0.5 mass % content of at least one sort of compounds chosen from a group which consists of phosphorus compounds expressed with the above-mentioned general formula (3) and

those metal salt, or amine salt by phosphorus element conversion.

[0013]As for a lubricating oil composition of this invention, it is preferred to contain at least one sort chosen from (E) non-ash powder medicine and the (F) antioxidant. As for a lubricating oil composition of this invention, it is preferred that sulfur content of lubricant base oil is below 0.005 mass %. As for a lubricating oil composition of this invention, it is preferred that sulfur content of a constituent is below 0.3 mass %. As for a lubricating oil composition of this invention, it is preferred that sulfur content is used for an internal-combustion engine which uses fuel below 50 mass ppm. As for a lubricating oil composition of this invention, being used for a gas engine is preferred.

[0014]

[Embodiment of the Invention]The 1st mode containing an ingredient (A), an ingredient (B), and an ingredient (C) and the 2nd mode containing an ingredient (A), an ingredient (B), and an ingredient (D) are contained in the lubricating oil composition of this invention. It is preferred that the ingredient (C) is further contained in the 2nd mode. Each ingredient contained in the constituent of each mode below is explained in order. Restriction in particular does not have the lubricant base oil in the lubricating oil composition of this invention, and the mineral oil system base oil and constructional system base oil which are used for the usual lubricating oil can be used for it. The lubricating oil fraction produced by carrying out distillation under reduced pressure of the ordinary pressure bottom oil specifically produced by carrying out atmospheric distillation of the crude oil as mineral oil system base oil, The thing which refined by performing one or more processings of solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, hydrotreating, etc. or wax isomerization mineral oil, the base oil manufactured by the technique of isomerizing GTL WAX (Gastouri kid wax), etc. can be illustrated. Although there is no restriction in particular, all the aromatic content of mineral oil system base oil is below 15 mass % preferably, and below 5 mass % is [below 10 mass %] below 2 mass % especially preferably still more preferably more preferably. Since oxidation stability is inferior when all the aromatic content of base oil exceeds 15 mass %, it is not desirable. All the above-mentioned aromatic content means the aromatic fraction (aromatic fraction) content measured based on ASTM D2549. In this aromatic fraction, usually, alkylbenzene, alkyl naphthalene, etc. The compound etc. which have hetero aromatic series, such as anthracene, phenanthrenes and these alkylation things, a compound that four or more rings of benzene rings condensed or pyridines, quinoline, phenols, and naphthols, are contained. Although there is no restriction in particular, as for the sulfur content in mineral oil system base oil, it is preferred that it is below 0.01 mass %, it is still more preferred that it is below 0.005 mass %, and it is preferred that it is especially below 0.001 mass %. By reducing the sulfur content of mineral oil system base oil, the lubricating oil composition which is more excellent in longed lane nature can be obtained.

[0015]As constructional system base oil, specifically Polybutene or its hydride; 1-octene oligomer, The Polly alpha olefin or its hydrides, such as 1-decene oligomer; A ditridecyl GURUTA rate, A di-2-ethylhexyl horse mackerel peat, di-isodecyl adipate, a ditridecyl horse mackerel peat, And diester, such as di-2-ethylhexyl sebacate; A trimethylolpropane KAPURI rate, Trimethylolpropane pelargonate, pentaerythritol 2-ethylhexanoate, And polyol esters, such as pentaerythritol pelargonate; aromatic system synthetic oil or these mixtures, such as alkyl naphthalene, alkylbenzene, and aromatic ester, etc. can be illustrated.

[0016]In this invention, the arbitrary mixture etc. of two or more sorts of lubricating oils chosen from the above-mentioned mineral oil system base oil, the above-mentioned constructional system base oil, or these can be used. For example, the mixed oil of one or more sorts of mineral oil system base oil, one or more sorts of constructional system base oil, one or more sorts of mineral oil system base oil, and one or more sorts of constructional system base oil, etc. can be mentioned.

[0017]Although the kinetic viscosity of lubricant base oil does not have restriction in particular, as for the kinetic viscosity in the 100 **, it is preferred that it is below 20 mm²/s, and it is below 10 mm²/s more preferably. On the other hand, as for the kinetic viscosity, it is preferred that it is more than 1 mm²/s, and it is more than 2 mm²/s more preferably. When the kinetic viscosity

in 100 ** of lubricant base oil exceeds 20 mm²/s, Since the low-temperature-viscosity characteristic gets worse, it is inferior to lubricity on the other hand since oil film formation in a lubrication point is insufficient when the kinetic viscosity is less than 1 mm²/s, and the evaporation loss of lubricant base oil becomes large, it is not desirable respectively.

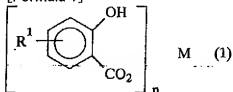
[0018]It is preferred that it is a NOACK amount of evaporation and is below 20 mass % as an amount of evaporation losses of lubricant base oil, it is still more preferred that it is below 16 mass %, and it is preferred that it is especially below 10 mass %. When the NOACK amount of evaporation of lubricant base oil exceeds 20 mass %, the evaporation loss of a lubricating oil oil is not only large, but, it is not desirable in order for there to be the sulfur compound and phosphorus compounds in a constituent, or a possibility that the amount of metal may deposit on a diesel-particulate filter with lubricant base oil and to be anxious about the adverse effect to exhaust gas purification performance. With a NOACK amount of evaporation here, the amount of evaporation after holding 60 g of lubricous oil samples under decompression of 250 ** and 150mmH₂O for 1 hour is measured.

[0019]Although the viscosity index of lubricant base oil does not have restriction in particular, as the viscosity characteristic outstanding from the low temperature to the elevated temperature is obtained, it is 100 or more that it is 80 or more desirable still more preferably, and the value is 120 or more still more preferably. Since the low-temperature-viscosity characteristic gets worse when the viscosity index is less than 80, it is not desirable.

[0020]It is an alkaline metal or alkaline-earth-metals salicylate, and salts, such as sodium of alkyl salicylic acid, potassium, magnesium, and calcium, are mentioned, and, specifically, the (A) ingredient in the lubricating oil composition of this invention has especially preferred salts, such as magnesium and calcium. For example, the compound expressed with a following general formula (1) can be mentioned.

[0021]

[Formula 7]



[0022]in a general formula (1) — R¹ — the carbon numbers 4-30 — the straight chain of 6-18 or the alkyl group of branching is shown preferably, and n shows 1 or 2 — M — an alkaline metal or alkaline-earth metals — desirable — calcium and magnesium — calcium is shown especially preferably. As an alkyl group expressed with the above-mentioned R¹. Specifically A butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, A nonyl group, a decyl group, an undecyl group, the dodecyl, a tridecyl group, a tetradecyl group, A pentadecyl group, a hexadecyl group, a heptadecyl group, an octadecyl group, A nonadecyl group, an icosyl group, a henicosyl group, a docosyl group, a tricosyl group, a tetracosyl group, a pentacosyl group, a hexacosyl group, a heptacosyl group, an octacosyl group, a nonacosyl group, a triacontyl group, etc. are mentioned. A straight chain or branching may be sufficient as these. The 1st class alkyl group, the 2nd class alkyl group, or the 3rd class alkyl group may be sufficient as these again.

[0023]The above-mentioned (A) ingredient is obtained by making the above-mentioned alkyl salicylic acid react to a base of a direct alkaline metal, alkaline metals, such as an oxide of alkaline-earth metals, and hydroxide, or alkaline-earth metals. Thus, by heating an obtained neutral (normal salt) alkaline metal or alkaline-earth-metals salicylate, superfluous alkali metal salt or alkaline earth metal salt, an alkali-metal-salt group, or an alkaline-earth-metal-salt group under existence of water. Under existence of a basic alkaline metal or alkaline-earth-metals salicylate, a neutral alkaline metal, or alkaline-earth-metals salicylate obtained, A persalt group nature (ultrabasic properties) alkaline metal or alkaline-earth-metals salicylate obtained by making hydroxide, carbon dioxide, boric acid, or borate salt of an alkaline metal or alkaline-earth

metals react is also contained.

[0024]As long as the (A) ingredient is prepared in this invention so that a metal ratio may become two or less, An above neutral alkaline metal or alkaline-earth-metals salicylate, basic alkaline metal or alkaline-earth-metals salicylate, and persalt group nature (ultrabasic properties) alkaline metal or alkaline-earth-metals salicylate can be used as one sort or two sorts or more of mixtures. In order to raise further base number maintenance nature at the time of being exposed to base number maintenance nature, especially NO_x atmosphere of a constituent obtained in this invention in an alkaline metal of the (B) ingredient, or combination with alkaline-earth-metals sulfonate, (A) It is preferred to make a metal ratio of an ingredient or less into 1.5, it is still more preferred to use 1.2 or less, and especially a thing for which being referred to as 1, i.e., a neutral alkaline metal, or alkaline-earth-metals salicylate is used is preferred. (A) Although a synergistic effect with the (B) ingredient is accepted to some extent when a metal ratio of an ingredient exceeds 2, the effect is smaller than an effect of this invention, and since the effect is hard to be acquired when especially the metal ratio exceeds 2.6, it is not preferred. With a metal ratio here, the valence x metallic element content (mol) / soap group of a metallic element. (Namely, alkyl salicylic acid group) It is expressed with content (mol), namely, a metal ratio shows an alkaline metal or alkaline-earth-metals content to alkyl salicylic acid group content in an alkaline metal or an alkaline-earth-metals salicylate system cleaning agent.

[0025]On a constituent whole-quantity standard, content of the (A) ingredient in a lubricating oil composition of this invention is more than 0.005 mass % in a metallic element equivalent unit, and more than 0.01 mass % is more than 0.02 mass % especially preferably preferably. On the other hand, it is preferred that the content is especially below [from a point that especially an effect acquired to content on a constituent whole-quantity standard although it is below 0.5 mass % in a metallic element equivalent unit and is below 0.2 mass % preferably is excellent] 0.06 mass %. (A) Since a synergistic effect with the (B) ingredient is not acquired as for a case of less than 0.005 mass %, and only an effect of balancing the content is not acquired on the other hand by the above-mentioned equivalent unit when the content exceeds 0.5 mass % by the above-mentioned equivalent unit, content of an ingredient is not preferred.

[0026]The (B) ingredient in a lubricating oil composition of this invention is an alkaline metal or alkaline-earth-metals sulfonate, and specifically for example, Neutral salt with the molecular weights 300-1500, alkyl aromatic sulfonic acid obtained by sulfonating alkyl aromatic compounds of 400-700 preferably, an alkaline metal, or alkaline-earth metals, Or it is obtained by heating the neutral salt concerned, a superfluous alkaline metal, alkaline earth metal salt, an alkali-metal-salt group, or an alkaline-earth-metal-salt group under existence of water, or making alkali earth metal hydroxide, carbon dioxide, and/or boric acid react under the neutral salt existence concerned. As an alkaline metal, as sodium, calcium, and alkaline-earth metals, magnesium, calcium, etc. are mentioned and especially calcium is preferred.

[0027]As the above-mentioned alkyl aromatic sulfonic acid, what is called petroleum sulfonic acid, synthetic sulfonic acid, etc. are specifically mentioned. What is called mahogany acid etc. that carry out a byproduction as petroleum sulfonic acid at the time of what generally sulfonated alkyl aromatic compounds of a lubricating oil fraction of mineral oil, or white oil manufacture are used. As synthetic sulfonic acid, carry out a byproduction from an alkylbenzene manufacturing plant which serves as a raw material of a detergent, for example, or, What sulfonated alkyl naphthalene, such as a thing which sulfonated alkylbenzene which has an alkyl group of straight chain shape and a letter of branching which are acquired by alkylating polyolefine with benzene, or dinonylnaphthalene, is used. Although there is no restriction in particular as a sulfonating agent at the time of sulfonating these alkyl aromatic compounds, fuming sulfuric acid and a sulfuric anhydride are usually used.

[0028](B) Although there is no restriction in particular, in order to acquire sufficient synergistic effect with the (A) ingredient, as for a metal ratio (shown by the same definitional equation as the above-mentioned (A) ingredient) of an ingredient, it is preferred that it is two or more, it is still more preferred that it is five or more, and it is preferred that it is especially eight or more. On the other hand, as for a metal ratio of the (B) ingredient, it is preferred that it is 25 or less, it is still more preferred that it is 20 or less, and it is preferred that it is especially 15 or less. That

mentioned. As the above-mentioned cycloalkyl group, a cycloalkyl group of the carbon numbers 5-7 of a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, etc. can be mentioned, for example. As the above-mentioned alkyl cycloalkyl group, For example, a methyl cyclopentyl group, a dimethyl cyclopentyl group, a methylethyl cyclopentyl group, A diethyl cyclopentyl group, a methylcyclohexyl group, a dimethyl cyclohexyl group, A methylethyl cyclohexyl group, a diethyl cyclohexyl group, a methyl cycloheptyl group, An alkyl cycloalkyl group (replacement positions to a cycloalkyl group of an alkyl group are also arbitrary) of the carbon numbers 6-11 of a dimethyl cycloheptyl group, a methylethyl cycloheptyl group, a diethyl cycloheptyl group, etc. can be mentioned.

[0037]As the above-mentioned alkenyl group, for example A butenyl group, a pentenyl group, a hexenyl group, A heptenyl group, an octenyl group, a nonenyl group, a decenyl group, an undecenyl group, Alkenyl groups (straight chain shape or a letter of branching may be sufficient as these alkenyl groups, and their position of a double bond is also arbitrary), such as a dodecenyl group, a tridecenyl group, a tetra decenyl group, a penta decenyl group, a hexa decenyl group, a heptadecenyl group, and an octadecenyl group, can be mentioned.

[0038]As the above-mentioned aryl group, aryl groups, such as a phenyl group and a naphthyl group, can be mentioned, for example. As the above-mentioned alkyl aryl group, for example A tolyl group, a xylyl group, An ethyl phenyl group, a propyl phenyl group, a butylphenyl group, a pentyl phenyl group, A hexyl phenyl group, a heptyl phenyl group, an octyl phenyl group, a nonylphenyl group, An alkyl aryl group (straight chain shape or a letter of branching may be sufficient as an alkyl group, and its replacement positions to an aryl group are also arbitrary) of the carbon numbers 7-18, such as a decyl phenyl group, an undecyl phenyl group, and a dodecyl phenyl group, can be mentioned. As the above-mentioned arylated alkyl group, for example Benzyl, a phenylethyl group, An arylated alkyl group (straight chain shape or a letter of branching may be sufficient as an alkyl group of these) of the carbon numbers 7-12, such as a phenylpropyl group, a phenylbutyl group, a phenylpentyl group, and a phenyl hexyl group, can be mentioned.

[0039]It is the alkyl groups of the carbon numbers 3-18 that they are an alkyl group of the carbon numbers 1-30 or an aryl group of the carbon numbers 6-24 desirable still more preferably, and a hydrocarbon group of the carbon numbers 1-30 expressed with the above-mentioned R^{11} - R^{16} is an alkyl group of the carbon numbers 4-10 still more preferably.

[0040]As phosphorus compounds expressed with a general formula (2), the following phosphorus compounds can be mentioned, for example. Phosphorous acid, monothiosphosphorous acid, dithiophosphorous acid; Phosphorous acid monoester which has one hydrocarbon group of the above-mentioned carbon numbers 1-30, Monothiosphosphorous acid monoester, dithiophosphorous acid monoester; Phosphorous acid diester which has two hydrocarbon groups of the above-mentioned carbon numbers 1-30, Monothiosphosphorous acid diester, dithiophosphorous acid diester; phosphorous acid triester [which has three hydrocarbon groups of the above-mentioned carbon numbers 1-30], monothiosphosphorous acid triester, and dithiophosphorous acid triester; and these mixtures. In this invention, it is preferred that two or more in X^1 of the above-mentioned general formula (2) - X^3 are an oxygen atom, and all three pieces are oxygen atoms more preferably.

[0041]As phosphorus compounds expressed with a general formula (3), the following phosphorus compounds can be mentioned, for example. Phosphoric acid, mono- thiophosphoric acid; Monoester phosphate which has one hydrocarbon group of the above-mentioned carbon numbers 1-30, Mono- thiophosphoric acid monoester, diester phosphate which has two hydrocarbon groups of the; above-mentioned carbon numbers 1-30, mono- thiophosphoric acid diester; trialkyl phosphate and mono- thiophosphoric acid triester; which has three hydrocarbon groups of the above-mentioned carbon numbers 1-30, and these mixtures. In this invention, all of X^4 of a general formula (3) - X^7 are oxygen atoms preferably.

[0042]As a salt of phosphorus compounds expressed with the general formula (2) or (3), To phosphorus compounds, metal bases, such as a metallic oxide, metal hydroxide, and metallic carbonate, Nitrogen compounds, such as an amine compound which has only a hydrocarbon group or a hydroxyl content hydrocarbon group of ammonia and the carbon numbers 1-30 in a

molecule, can be made to be able to act, and a salt which neutralized a part or all of acid water matter that remains can be mentioned.

[0043]Specifically as metal in the above-mentioned metal base, heavy metals, such as alkaline-earth metals, such as alkaline metals, such as lithium, sodium, potassium, and caesium, calcium, magnesium, and barium, zinc, copper, iron, lead, nickel, silver, manganese, and molybdenum, are mentioned. In these, alkaline-earth metals, such as zinc, molybdenum, and calcium, are preferred. It is thought that a complex which the coordination numbers of phosphorus compounds differ as metal salt of the above-mentioned phosphorus compounds according to a metal valence, for example, two phosphorus compounds configure to one metal atom in divalent zinc and calcium is formed.

[0044]Specifically as the above-mentioned nitrogen compound, ammonia, monoamine, diamine, and polyamine are mentioned. More specifically Methylamine, ethylamine, propylamine, a butylamine, Pentylamine, hexylamine, heptyl amine, octylamine, Nonyl amine, decyl amine, undecyl amine, dodecyl amine, Tridecyl amine, tetradecylamine, pentadecyl amine, hexadecyl amine, Heptadecyl amine, octadecyl amine, dimethylamine, diethylamine, Dipropyl amine, dibutyl amine, dipentylamine, dihexyl amine, Diheptylamine, dioctyl amine, dinonyl amine, didecyl amine, Diundecyl amine, didodecyl amine, ditridecyl amine, ditetradecyl amine, Dipentadecyl amine, dihexadecyl amine, diheptadecyl amine, Dioctadecyl amine, methylethyl amine, methylpropyl amine, Alkylamine which has an alkyl group (straight chain shape or a letter of branching may be sufficient as an alkyl group of these) of the carbon numbers 1-30, such as methylbutyl amine, ethyl propylamine, an ethyl butylamine, and a propyl butylamine;

[0045]Ethenyl amine, propenyl amine, butenyl amine, octenyl amine, And alkenyl amine which has an alkenyl group (straight chain shape or a letter of branching may be sufficient as an alkenyl group of these) of the carbon numbers 2-30, such as oleylamine; Methanol amine, Ethanolamine, propanolamine, butanol amine, pentanol amine, Hexanol amine, heptanol amine, octanol amine, nonanol amine, Methanol ethanolamine, methanol propanolamine, methanol butanol amine, Alkanolamine which has an alkanol group (straight chain shape or a letter of branching may be sufficient as an alkanol group of these) of the carbon numbers 1-30, such as ethanol propanolamine, ethanol butanol amine, and propanol butanol amine;

[0046]Alkylene diamine which has an alkylene group of the carbon numbers 1-30, such as methylenediamine, ethylenediamine, propylenediamine, and butylenediamine; Diethylenetriamine, Polyamine, such as triethylenetetramine, tetraethylenepentamine, and pentaethylenhexamine; Undecyldiethylamine, Undecyldiethanolamine, dodecyl dipropanolamine, oleyldiethanolamine, The above-mentioned monoamines, such as oleylpropylenediamine and stearyl tetraethylenepentamine, Heterocyclic compounds which have an alkyl group or an alkenyl group of the carbon numbers 8-20 in diamine and polyamine, such as a compound and N-hydroxyethyl oleylimidazoline; alkylene oxide addition [of a compound of these]; these mixtures, etc. can be illustrated. Also in these nitrogen compounds, decyl amine, dodecyl amine, tridecyl amine, It can mention as an example with preferred fatty amine (straight chain shape or a letter of branching may be sufficient as these) which has an alkyl group or alkenyl groups of the carbon numbers 10-20, such as heptadecyl amine, octadecyl amine, oleylamine, and stearylamine.

[0047]Phosphorous acid diester which has an alkyl group or two aryl groups of the carbon numbers 3-18 in these (C) ingredients, and zinc, Molybdenum, calcium, or a salt with alkenyl amine of the carbon numbers 2-20, Phosphorous acid triester which has an alkyl group or three aryl groups of the carbon numbers 3-18, It is preferred that it is trialkyl phosphate which has an alkyl group or three aryl groups of a salt with diester of phosphoric acid which has an alkyl group or two aryl groups of the carbon numbers 3-18, zinc, molybdenum, calcium, or alkenyl amine of the carbon numbers 2-20, or the carbon numbers 3-18. These (C) ingredients can blend arbitrarily one kind or two kinds or more.

[0048]In a lubricating oil composition of this invention, content of the (C) ingredient, On a constituent whole-quantity standard, are more than 0.005 mass % as a phosphorus element equivalent unit, and preferably, are more than 0.05 mass % preferably, and, on the other hand, more than 0.02 mass % the content, It is below 0.5 mass %, is below 0.2 mass % preferably, and is below 0.1 mass % especially preferably. (C) When a case of less than 0.005

mass % is ineffective to abrasion resistance as a phosphorus element and content of an ingredient exceeds 0.5 mass %, in order to be anxious about an adverse effect to an exhaust gas aftertreatment apparatus by Lynn, it is not desirable respectively.

[0049] Although it can be made to contain within the limits of the above-mentioned amount of phosphorus elements also about a compound which contains sulfur among the above-mentioned (C) ingredients in this invention, preferably, the content is a sulfur element equivalent unit, is below 0.1 mass %, and is below 0.08 mass % still more preferably. In order to raise extremely base number maintenance nature under NOx atmosphere, it is most preferred not to contain a compound containing sulfur.

[0050] The (D) ingredient in a lubricating oil composition of this invention is dithiophosphate zinc (ZDTP). As dithiophosphate zinc (ZDTP), specifically, Dipropyl dithiophosphate zinc, dibutyl dithiophosphate zinc, dipentyl dithiophosphate zinc, The carbon numbers 3-18 of dihexyl dithiophosphate zinc, diheptyl dithiophosphate zinc, dioctyl dithiophosphate zinc, etc., dialkyl phosphorodithioate zinc which has straight chain shape or a letter alkyl group of branching of the carbon numbers 3-10 preferably; Diphenyldithiophosphate zinc, And the carbon numbers 6-18 of ditolyl dithiophosphate zinc etc., JI (alkyl) (aryl) dithiophosphate zinc which has an aryl group or an alkyl aryl group of the carbon numbers 6-10 preferably, these mixtures, etc. are mentioned.

[0051] Although it is generally publicly known to usually raise oxidation stability under NOx atmosphere as a peroxide decomposition agent as for the (D) ingredient in this invention, in order to raise the outstanding base number maintenance characteristic like this invention, few things of the content are preferred. For this reason, on a constituent whole-quantity standard, content of the (D) ingredient is below 0.1 mass % in a sulfur element equivalent unit, and below 0.09 mass % is below 0.08 mass % still more preferably. Especially when it does not contain the (D) ingredient, a constituent excellent in base number maintenance nature under NOx atmosphere can be obtained.

[0052] It is preferred that at least one sort of additive agents chosen from a group which becomes a lubricating oil composition of this invention from (E) non-ash powder medicine and the (F) antioxidant further contain.

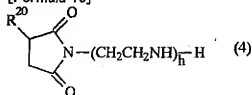
[0053] (E) Although arbitrary non-ash powder medicine used for a lubricating oil can be used as non-ash powder medicine, For example, a nitrogen-containing compound which has an alkyl group or an alkenyl group of a straight chain of the carbon numbers 40-400 or a letter of branching in [at least one] a molecule, its derivative, or a denaturation article of alkenyl succinimid is mentioned. One kind arbitrarily chosen out of these or two kinds or more can be blended, a carbon number of this alkyl group or an alkenyl group -- 40-400 -- it is 60-350 preferably. Since the cold-temperature fluidity of a lubricating oil composition gets worse when solubility over lubricant base oil of a compound falls when a carbon number of an alkyl group or an alkenyl group is less than 40, and a carbon number of an alkyl group or an alkenyl group exceeds 400 on the other hand, it is not desirable respectively. Although straight chain shape or a letter of branching may be sufficient as this alkyl group or alkenyl group, as a desirable thing, Specifically, a letter alkyl group of branching, a letter alkenyl group of branching, etc. which are derived from oligomer of olefins, such as propylene, 1-butene, and isobutylene, or co-oligomer of ethylene and propylene are mentioned. (E) although a nitrogen content of a nitrogen-containing compound quoted as one example of an ingredient is arbitrary -- from points, such as abrasion resistance and oxidation stability, -- usually -- the nitrogen content -- 0.01 to 10 mass % -- it is a thing of 0.1 - 10 mass % preferably.

[0054] (E) As an ingredient being concrete, the following compound is mentioned, for example. One sort or two sorts or more of compounds chosen from ***** can be used.

(E-1) Succinimid which has an alkyl group or an alkenyl group of the carbon numbers 40-400 in [at least one] a molecule, Or benzylamine which has an alkyl group or an alkenyl group of the derivative (E-2) carbon numbers 40-400 in [at least one] a molecule, Or polyamine which has an alkyl group or an alkenyl group of the derivative (E-3) carbon numbers 40-400 in [at least one] a molecule or its derivative [0055] More specifically as the above-mentioned (E-1) succinimid, a compound etc. which are shown by a following general formula (4) and a general formula (5) can be illustrated.

[0056]

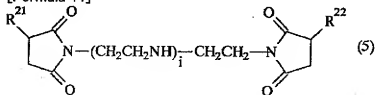
[Formula 10]



[0057]in a general formula (4) — R^{20} — the carbon numbers 40–400 — the alkyl group or alkenyl group of 60–350 is shown preferably — h — 1–5 — the integer of 2–4 is shown preferably.

[0058]

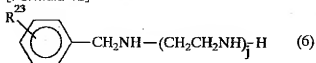
[Formula 11]



[0059]As for R^{21} and R^{22} , in a general formula (5), it is individually preferred respectively the carbon numbers 40–400 and that the alkyl group or alkenyl group of 60–350 is shown preferably, and it is a polybutenyl group. i — 0–4 — the integer of 1–3 is shown preferably. Although the succinimid of what is called a monotype expressed with the formula (4) which the succinic anhydride added to the end of polyamine, and what is called a screw type of succinimid expressed with the formula (5) which the succinic anhydride added to the both ends of polyamine are contained in succinimid, Those any or these mixtures may be contained in the constituent of this invention. The process of such succinimids can be acquired by making the alkyl or alkenyl succinic acid which obtained it by making the alkyl group or alkenyl group of the carbon numbers 40–400 react to a maleic anhydride at 100–200 °C, for example react to polyamine, although there is no restriction in particular. Specifically as polyamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine, etc. can be illustrated. [0060]More specifically as the above-mentioned (E-2) benzylamine, a compound etc. which are expressed with the following general formula (6) can be illustrated.

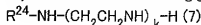
[0061]

[Formula 12]



[0062]in a general formula (6) — R^{23} — the carbon numbers 40–400 — the alkyl group or alkenyl group of 60–350 is shown preferably — j — 1–5 — the integer of 2–4 is shown preferably. Although the manufacturing method of this benzylamine is not limited at all. For example, after making polyolefines, such as a propylene oligomer, polybutene, and an ethylene-alpha olefin copolymer, react to phenol and considering it as alkylphenol, It can obtain by making polyamine, such as formaldehyde, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and pentaethylenhexamine, react to this by a Mannich reaction.

[0063]More specifically as the above-mentioned (E-3) polyamine, the compound etc. which are expressed with the following general formula (7) can be illustrated.



[0064]in a general formula (7) — R^{24} — the carbon numbers 40–400 — an alkyl group or an alkenyl group of 60–350 is shown preferably — k — 1–5 — an integer of 2–4 is shown preferably. Although a manufacturing method of this polyamine is not limited at all. For example,

after chlorinating polyolefines, such as a propylene oligomer, polybutene, and an ethylene- α -olefin copolymer, it can obtain by making polyamine, such as ammonia, ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and pentaethylenhexamine, react to this.

[0065]As a derivative of a nitrogen-containing compound quoted as one example of the (E) ingredient, To the concrete for example, above-mentioned nitrogen-containing compound, monocarboxylic acid (fatty acid etc.) and oxalic acid of the carbon numbers 1-30, Polycarboxylic acid of the carbon numbers 2-30 of phthalic acid, trimellitic acid, pyromellitic acid, etc. is made to act, Neutralize a part or all of an amino group and/or an imino group which remain, or, What is called an amidated acid denaturation compound; Boric acid is made to act on the above-mentioned nitrogen-containing compound, Neutralize a part or all of an amino group and/or an imino group which remain, or, What is called an amidated boron denaturation compound; denaturation compound; etc. which combined two or more sorts of denaturation chosen as sulfur denaturation compound; and the above-mentioned nitrogen-containing compound which made a sulfur compound act on the above-mentioned nitrogen-containing compound from acid denaturation, boron denaturation, and sulfur denaturation are mentioned. It is effective, in order that a boric acid conversion compound of alkenyl succinimid may be excellent in heat resistance and antioxidizing nature and may improve base number maintenance nature more also in a lubricating oil composition of this invention also in these derivatives.

[0066]When making the (E) ingredient contain in a lubricating oil composition of this invention, the content is usually a lubricating oil composition whole-quantity standard, is 0.01 - 20 mass %, and is 0.1 - 10 mass % preferably. (E) When content of an ingredient is less than 0.01 mass %, there are few effects over base number maintenance nature under NO_x atmosphere, and since the cold-temperature fluidity of a lubricating oil composition gets worse substantially on the other hand when exceeding 20 mass %, it is not desirable respectively.

[0067]It is usable if it is generally used to lubricating oils, such as a phenolic antioxidant, an amine system antioxidant, a metal system antioxidant, as an antioxidant (F). Since addition of an antioxidant improves the antioxidizing nature of a lubricating oil composition more, by it, base number maintenance nature in this invention can be improved more. As a phenolic antioxidant, for example 4,4'-methylenebis (2,6-di-tert-butylphenol), A 4,4'-screw (2,6-di-tert-butylphenol), a 4,4'-screw (2-methyl-6-tert-butylphenol), 2,2'-methylenebis (4-ethyl-6-tert-butylphenol), 2,2'-methylenebis (4-methyl-6-tert-butylphenol), 4,4'-butylidenebis (3-methyl-6-tert-butylphenol), A 4,4'-isopropylidenescrew (2,6-di-tert-butylphenol), 2,2'-methylenebis (4-methyl-6-nonyl phenol), a 2,2'-isobutylidenescrew (4,6-dimethylphenol), 2,2'-methylenebis (4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methyl phenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert-alpha-dimethylamino p-cresol, the 2,6-di-tert-butyl-4-(N,N'-dimethylamino methyl phenol), 4,4'-Thiobis (2-methyl-6-tert-butylphenol), 4,4'-Thiobis (3-methyl-6-tert-butylphenol), 2,2'-Thiobis (4-methyl-6-tert-butylphenol), A bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)sulfide, A bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, A 2,2'-thio-diethylenescrew [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], Tridecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, Pentaerythrityl tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate and 3-methyl-5-tert-butyl-4-hydroxyphenyl substitution fatty acid ester can be mentioned as a desirable example. These may mix and use two or more sorts.

[0068]As an amine system antioxidant, phenyl-alpha-naphthylamine, alkylphenyl alpha-naphthylamine, and dialkyl diphenylamine can be mentioned, for example. These may mix and use two or more sorts. The above-mentioned phenolic antioxidant and an amine system antioxidant may be combined and blended.

[0069]When making the (F) ingredient contain in a lubricating oil composition of this invention, the content is usually below 5.0 mass % on a lubricating oil composition whole-quantity standard, is below 3.0 mass % preferably, and is below 2.5 mass % still more preferably. When the content exceeds 5.0 mass %, since sufficient antioxidizing nature corresponding to loadings is not obtained, it is not desirable. On the other hand, in order to improve more base number maintenance nature in a lubricating oil deterioration process, on a lubricating oil composition

whole-quantity standard, the content is more than 0.1 mass % preferably, and is more than 1 mass % preferably.

[0070] Although a lubricating oil composition of this invention is excellent in base number maintenance nature under NO_x atmosphere, in order to raise the performance further, it can add arbitrary additive agents generally used to a lubricating oil according to the purpose. As such an additive agent, additive agents, such as antiwear agents other than metal system cleaning agents other than a viscosity index improver, the (A) ingredient, and the (B) ingredient, the (C) ingredient, and the (D) ingredient, a friction modifier, corrosion inhibitor, a rust-proofer, a demulsifier, a metal deactivator, a defoaming agent, and colorant, etc. can be mentioned, for example.

[0071] What is called non-distributed viscosity index improvers, such as a polymer of one sort or two sorts or more of monomers or a copolymer specifically chosen from various methacrylic acid ester as a viscosity index improver, or its hydrogenation thing, Or what is called a distributed viscosity index improver to which copolymerization of the various methacrylic acid ester which contains a nitrogen compound further was carried out, non-distributed type or a distributed ethylene- α olefin copolymer (as α olefin — propylene.) Or it can illustrate 1-butene, 1-pentene, etc., the hydride, polyisobutylene or its hydrogenation thing, a hydride of a styrene diene copolymer, a styrene maleic-anhydride-ester copolymer, poly alkyl styrene, etc. are mentioned.

[0072] A molecular weight of these viscosity index improvers needs to select in consideration of shear stability. Specifically a number average molecular weight of a viscosity index improver, For example, in the case of distributed type and non-distributed polymethacrylate, 5,000-1,000,000 — a thing of 100,000-900,000 preferably, [usually,] a case of polyisobutylene or its hydride — usually — 800-5,000 — desirable — a thing of 1,000-4,000 — a case of an ethylene α olefin copolymer or its hydride — usually — 800-500,000 — a thing of 3,000-200,000 is used preferably. Especially when an ethylene α olefin copolymer or its hydride is used also in these viscosity index improvers, a lubricating oil composition excellent in shear stability can be obtained. One kind or two kinds or more of compounds arbitrarily selected out of the above-mentioned viscosity index improver can be made to contain in an arbitrary quantity. Content of a viscosity index improver is usually 0.1 to 20.0 mass % on a lubricating oil composition standard. Although a viscosity index improver generally worsens an elevated-temperature detergency, when not making a viscosity index improver contain, in the case of few content (for example, below 1 mass %), a constituent which has the outstanding elevated-temperature detergency can be obtained.

[0073] (A) As metal system cleaning agents other than an ingredient and the (B) ingredient, an alkaline metal or alkaline-earth-metals salicylate etc. in which an alkaline metal or alkali earth metal phenate, and a metal ratio exceed 2 is mentioned.

[0074] (C) As antiwear agents other than an ingredient and the (D) ingredient, sulfur content compounds, such as disulfide, olefins sulfide, sulfurized oil fat, and zinc dithiocarbamate, etc. are mentioned, for example.

[0075] As a friction modifier, molybdenum dithiocarbamate, dithiophosphate molybdenum, molybdenum disulfide, long chain fatty amine, long chain fatty acid, long-chain-fatty-acid ester, long-chain-fatty-acid amide, long-chain aliphatic alcohol, etc. are mentioned, for example.

[0076] As corrosion inhibitor, a benzotriazole system, a tolyltriazole system, a thiadiazole system, an imidazole series compound, etc. are mentioned, for example.

[0077] As a rust-proofer, petroleum sulfonate, alkyl benzene sulfonate, dinonylnaphthalene sulfonate, alkenyl succinate, multivalent alcohol ester, etc. are mentioned, for example.

[0078] As a demulsifier, polyalkylene glycol system non-ion system surface-active agents, such as polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, and polyoxyethylene alkyl naphthyl ether, etc. are mentioned, for example.

[0079] As a metal deactivator, for example Imidazoline, a pyrimidine derivative, Alkyl thiadiazole, mercaptobenzothiazole, benzotriazol, or its derivative, 1,3,4-thiadiazole polysulfide, 1,3,4-thiadiazolyl 2,5-screw dialkyl dithiocarbamate, 2-(alkyl dithio) benzimidazole, beta-(α -carboxybenzylthio) propione nitril, etc. are mentioned.

[0080]As a defoaming agent, silicone, a full OROSHI recall, fluoro alkyl ether, etc. are mentioned, for example.

[0081]In making a lubricating oil composition of this invention contain these additive agents, The content is a lubricating oil composition whole-quantity standard, and Metal system cleaning agents other than the (A) ingredient and the (B) ingredient, (C) In antiwear agents other than an ingredient and the (D) ingredient, a friction modifier, corrosion inhibitor, a rust-proofer, and a demulsifier, choose by 0.005 - 5 mass %, and it is chosen by 0.005 - 1 mass % in a metal deactivator, and is usually chosen in the range of 0.0005 - 1 mass % with a defoaming agent, respectively.

[0082]an antiwear agent (a compound which contains sulfur among the (C) ingredients,) in which a lubricating oil composition of this invention contains sulfur with the above-mentioned (D) ingredient (ZDTP) Disulfide, olefins sulfide, sulfurized oil fat, and zinc dithiocarbamate, Or a friction modifier containing sulfur, such as molybdenum dithiocarbamate and dithiophosphate molybdenum, etc., (B) It is preferred to restrict a total content of a sulfur content additive agent except an ingredient, and a total content of an above-mentioned sulfur content antiwear agent on a constituent whole-quantity standard. It is preferred that below 0.1 mass % carries out at a sulfur element equivalent unit, it is more preferred that below 0.09 mass % carries out, and it is still more preferred that below 0.08 mass % carries out. By restricting content of a sulfur content additive agent as mentioned above, it becomes possible to improve longed lane performance more. A case where dilution oils (for example, solvent refining mineral oil etc.) for improving handling of a solvent and an additive agent which are used when compounding an additive agent are contained is common on a commercial additive agent, and a sulfur content additive agent here does not mean a sulfur compound resulting from these solvents or a dilution oil.

[0083]Even if sulfur content resulting from these solvents or a dilution oil contains in this invention, Below 0.3 mass % can carry out total sulfur part content in a constituent, Advanced hydrocracking base oil whose sulfur content content is below 0.005 mass % about these solvents or a dilution oil, If synthetic oil, such as base oil manufactured by the technique of having isomerized GTL Wax (Gastaut liquid wax) which does not contain sulfur content substantially, etc. are used, Since it can be considered as a constituent which can furthermore reduce sulfur content, is excellent in base number maintenance nature under NOx atmosphere, and can aim at performance maintenance of a diesel-particulate filter, it is more desirable. Below as for 0.2 mass %, especially in this invention, a constituent below 0.1 mass % is obtained for a part for total sulfur in a constituent.

[0084]Although a lubricating oil composition of this invention can be preferably used as internal combustion engine oil, such as gasoline engines, such as a two-wheeled vehicle, a four-wheeled vehicle, an object for power generation, and for ships, a diesel power plant, and a gas engine, Low sulfur fuel, for example, sulfur content, still more preferably below 50 mass ppm Below 30 mass ppm. especially --- desirable --- gasoline and gas oil below 10 mass ppm, kerosene, or sulfur content --- fuel (LPG.) below 1 mass ppm It can be especially used preferably as internal combustion engine oil using hydrogen, wood ether and alcohol which do not contain natural gas and sulfur content substantially, GTL (Gastouri kid) fuel, etc., especially a lubricating oil for gas engines. A lubricating oil composition of this invention only not only in base number maintenance nature under NOx atmosphere, A lubricating oil in which it excels in high-temperature-oxidation stability, abrasion resistance, an elevated-temperature detergency, etc., and such performance is demanded, For example, it can be automatic or can be conveniently used also as lubricating oils, such as lubricating oils for drive systems, such as a manual transmission, a wet oiling brake, hydraulic oil, turbine oil, compressor oil, a bearing oil, and refrigerating machine oil.

[0085]

[Example]Although an example and a comparative example explain the contents of this invention still more concretely below, this invention is not limited to these examples at all.

[0086](Examples 1-2 and comparative examples 1-5) As shown in Table 1, the lubricating oil composition (examples 1-3) of this invention, the lubricating oil composition for reference (reference examples 1-2), and the lubricating oil composition for comparison (comparative examples 1-3) were prepared, respectively.

[0087]

[Table 1]

	実施例1	実施例2	実施例3	比較例1	参考例1	比較例2	比較例3
水素を換算基準 ¹⁾	質量%	残部	残部	残部	残部	残部	残部
(A) Caサリシレート ²⁾	質量%	2.0	2.0	2.0	13.3	—	—
金属元素換算量	質量%	(0.04)	(0.04)	(0.04)	(0.28)	—	—
(B) Caスルホネート ³⁾	質量%	2.0	2.0	2.0	—	2.3	—
金属元素換算量	質量%	(0.24)	(0.24)	(0.24)	—	(0.28)	—
硫黄元素換算量	質量%	(0.03)	(0.03)	(0.03)	—	(0.03)	—
Caサリシレート ⁴⁾	質量%	—	—	—	—	4.5	—
金属元素換算量	質量%	—	—	—	—	(0.28)	—
Caフェネート ⁵⁾	質量%	—	—	—	—	—	3.6
金属元素換算量	質量%	—	—	—	—	—	(0.28)
硫黄元素換算量	質量%	—	—	—	—	—	(0.12)
(C) リン含有率40%防止剤 ⁶⁾	質量%	0.8	—	0.3	—	0.6	—
リン元素換算量	質量%	(0.08)	—	(0.04)	—	(0.06)	—
硫黄元素換算量	質量%	(0.03)	—	(0.00)	—	(0.00)	—
(D) ジフェニルジホスフェート ⁷⁾	質量%	—	0.55	0.58	1.1	—	1.1
硫黄元素換算量	質量%	—	(0.06)	(0.08)	(0.16)	—	(0.16)
(E) 無灰分防止剤 ⁸⁾	質量%	5.0	5.0	5.0	5.0	5.0	5.0
リン酸化合物 ⁹⁾	質量%	2.0	2.0	2.0	2.0	2.0	2.0
硫黄元素換算量	質量%	4.0	4.0	4.0	4.0	4.0	4.0
硫黄元素換算量	質量%	0.01	0.01	0.01	0.01	0.01	0.01
硫黄元素換算量	質量%	0.04	0.12	0.12	0.20	0.04	0.17
NO _x 吸収試験(135℃)後の塩基価残存率(HOI法) %	52	80	83	65	76	90	68
% 48時間後	65	35	40	17	24	20	18

1) 芳基換分1.2%, 硫黄分10質量ppm, 100℃動粘度: 5.6mm²/s, 粘度指数: 125, NOACK消費量: 8質量%

2) Ca含有量: 23質量%, 金属比: 1.0, 硫黄含有量: 0.6質量%

3) Ca含有量: 12.5質量%, 金属比: 1.0, 硫黄含有量: 0.6質量%

4) Ca含有量: 8.5質量%, 金属比: 2.7, 硫黄含有量: 0.0質量%

5) Ca含有量: 8.0質量%, 硫黄含有量: 3.3質量%

6) ジブチルリン酸塩: (リン含有量: 13.2質量%, 硫黄含有量: 0.0質量%)

7) ジ(1, 3-ジブチルブチル)ジフェニルジホスフェート: (リン含有量: 7.2質量%, 硫黄含有量: 14.4質量%)

8) ポリ(2-メチル-2-プロピル-5-フェニル-5-ヒドロキシ-5-フェニル)プロピオネート及びアルキルジフェニルアミン(1:1:1)

9) オクテール-3-ol, 3-ブチル-2-ヒドロキシ-2-フェニル-2-プロピオネート及びアルキルジフェニルアミン(1:1:1)

10) OGP 平均分子量: 16万

11) ポリアルキルグリコール系

6) 構造式



7) 構造式



[0088] The following performance evaluation test was done to the obtained class product. The result is shown in Table 1.

(Aging of the total basicity by a NOx absorption test) NOx gas was blown into test oil on the conditions (135 °C, NOx: 1185 ppm) based on the Japanese tribology meeting proceedings-1992, 10, and 465, and aging of the total basicity (hydrochloric acid method) when carrying out forcible degradation was measured. It is shown that it is a longed lane oil which base number maintenance performance is high and can use more for a long time under a NOx existence which is used with an internal-combustion engine, so that reduction in the total basicity is small.

[0089] In the passage clear from Table 1, the lubricating oil composition of this invention shows the base number maintenance nature which was extremely excellent under NOx atmosphere. It turns out that the constituent (example 1) which does not contain ZDTP in particular but contains dialkyl zinc phosphate (ZP) shows the extremely outstanding base number maintenance nature.

The base number maintenance nature outstanding enough also in the constituent (example 2) as for which below 0.1 mass % carried out content of ZDTP by the sulfur element equivalent unit is shown. And these examples can improve the base number maintenance characteristic further compared with the case (reference examples 1 and 2) where salicylate or sulfonate is independently used as a metal system cleaning agent, respectively.

[0090] When the antiwear agent (dialkyl zinc phosphate (ZP)) in the constituent of Example 1 is transposed to ZDTP (it is 0.16 mass % at a sulfur element equivalent unit) on the other hand (comparative example 1), When the metal system cleaning agent of the constituent of the comparative example 1 is changed to persalt group nature salicylate excellent in base number maintenance nature (comparative example 2: the conventional longed lane oil), And in the case (comparative example 3) where the metal system cleaning agent of the constituent of Example 1 is changed to persalt group nature phenate, it turns out that the base number maintenance characteristic inferior to the constituent of this invention is shown.

[0091] It is checking that the constituent of Examples 1-3 has the elevated-temperature

detergency which has the abrasion preventing performance outstanding also in the abrasion preventing performance evaluation test, and was extremely excellent also in not less than 300 ** especially in the hot tube examination. What it has the outstanding performance with the same said of the constituent containing the (C) ingredient except having mentioned to the example for, it is checking that the performance to which the zinc salt of mono- thiophosphoric acid diester, diester phosphate and its calcium salt or oleyl amine salt, the constituent containing trialkyl phosphate, etc. rank second to the constituent containing ZP especially is shown.

[0092]

[Effect of the Invention]In spite of the lubricating oil composition of this invention reducing the sulfur content additive agent which has the antioxidant performance as a peroxide decomposition agent like ZDTP or not using it for it at all, It also has the abrasion preventing performance and elevated-temperature clarification performance which raised antioxidizing nature extremely, excelled in the base number maintenance nature under NOx atmosphere, i.e., longed lane performance, extremely, and it excelled further. Since the lubricating oil composition of this invention can hold down the total sulfur part content low to below 0.3 mass %, it can reduce poisoning with sulfur to an exhaust gas cleaning catalyst etc., and it can be used for it conveniently for the engine equipped with exhaust gas aftertreatment apparatus, such as an exhaust gas cleaning catalyst. The lubricating oil composition of this invention becomes possible [developing longed lane performance further], and can contribute to a waste oil problem, saving resources, etc. because the above sulfur content applies to the engine which uses the fuel below 50 mass ppm, especially a gas engine. The lubricating oil composition of this invention Base number maintenance nature, the lubricating oil for which abrasion preventing performance and an elevated-temperature detergency are needed further, For example, it can be automatic or can be conveniently used also as lubricating oils, such as lubricating oils for drive systems, such as a manual transmission, a wet oiling brake, hydraulic oil, turbine oil, compressor oil, a bearing oil, and refrigerating machine oil.

[Translation done.]